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The Catalytic Activity of Cu_2O Microparticles

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***Abstract*—**Copper (I) oxide microparticles with the morphology of cubic and hollow sphere were synthesized with the assistance of surfactant as the shape controller. Both particles were then subjected to study the catalytic activity and observed the results of shape effects of catalysts on rate of catalytic reaction. The decolorizing reaction of crystal violet and sodium hydroxide was chosen and measured the decreasing of reactant with respect to times using spectrophotometer. The result revealed that morphology of crystal had no effect on the catalytic activity for crystal violet reaction but contributed to total surface area predominantly.

***Keywords*—**Copper (I) oxide, Catalytic activity, Crystal violet.

I. Introduction

COPPER (I) oxide particles have been focused by many research works because of its unique material properties and potential applications in semiconductor electronics [1], photocatalysis and catalysis [2], [3], conductive inks [4]. A variety shape of Cu_2O particle has been attempted to synthesize with the simple processes such as cube, triangle, hexapod, octapod, hollow sphere etc. [5]-[9]. The usage of Cu_2O as the high performance for photocatalytic reaction was also published worldwide [10]-[13]. The interesting results was published by Ho, J and Huang, M. H. [10] who studied the photocatalytic activity of Cu_2O for various shape and found that shape of particle paid their important role for photocatalytic reaction.

As mentioned above that many research works focused on the photocatalytic activity of Cu_2O but less of them were studied for its catalytic activity. Thus, this work aimed to study the catalytic activation of copper (I) oxide with different shapes of cube, sphere, and hollow sphere. This may confirm the promising material of Cu_2O in both catalytic and photocatalytic activities.

The preparation of Cu_2O was synthesized via methods published by [14]. The rate of the reaction between crystal violet and NaOH will be examined with and without the presence of Cu_2O. A UV-spectrophotometer was used to monitor the crystal violet concentration as a function of time.

The reaction between crystal violet and NaOH was shown stoichiometry in Fig. 1.

It was known as a pseudo first reaction rate [15]. Because NaOH and products was colorless except for crystal violet, rate of reaction was observed with respect to the decolrization of crystal violet which has an intense violet color. During the course of the reaction, the reaction mixture color becomes less and less intense, ultimately becoming colorless when all of the crystal violet has been consumed. The rate of the crystal violet/NaOH reaction is given by the following generalized power-law rate expression.

$$\text{Rate} = k[OH^-]^m[CV]^n \quad (1)$$

k is the rate constant for the reaction. CV is an abbreviation for crystal violet, m and n are the reaction order with respect to OH^- and CV, respectively. In this experiment, the initial $[OH^-]$ is made much greater than the initial [CV]. Thus, the $[OH^-]$ change, during the time that the CV is consumed, is negligible. For this reason, $[OH^-]$ can be treated as a constant and n in (1) can be written as,

$$\text{Rate} = k'[CV]^n \quad (2)$$

where $k' = k[OH^-]^m$. k' is termed a pseudo rate constant. The combined form of the pseudo rate law in (2) depends on the reaction order with respect to CV. The integrated rate laws for first order reaction are given in (3). Rearrange in linear equation form, y = mx + b.

$$\ln\frac{[CV]_t}{[CV]_o} = kt \quad (3)$$

The first term based on the absorption by the samples. The concentration of CV and color intensity decrease as the reaction proceeds and the absorbance will also decrease.

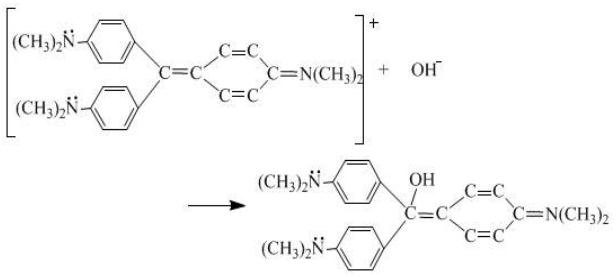

Fig. 1 Stoichiometry of reaction between crystal violet and NaOH

II. Experimental

A. Synthesis and Characterization of Cu_2O Microcrystals

Copper sulfate pentahydrate and ascorbic acid were of analytical grade purchased from J.T.Baker Co. Ltd. Polyoxyethylene (5) nonylphenyl ether (PONPE-5), Sodium dodecylsulfate (SDS) were purchased from Fluka Chemicals. Absolute ethanol was obtained from Mallinckrodt Chemicals.

The preparation of Cu_2O was conducted by mixing 30 mL of 50 mM surfactant, PONPE-5 or SDS, with 3 mL of 0.5 M

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$CuSO_4$ then pH was adjust to 7 with NaOH 1M and NaOH 0.1M, and added 2 mL of ascorbic acid. The mixed solution was then subjected to a temperature controllable sonicator for 3h at 40°C. The precipitation was collected, washed extensively with distilled water and absolute ethanol and finally dried at 70°C overnight.

Powder X-ray diffraction (XRD) patterns were recorded on a D8 Advance-Bruker instrument using CuK_α ($\lambda = 0.1549$ nm) radiation. Fourier transform infrared (FT-IR) spectra were obtained in 4000–400 cm^{-1} range on a FT/IR spectrometer. The morphology of Cu_2O was examined by Scanning Electron Microscopy (SEM). TEM images were collected on a Hitachi Model H-800 transmission electron microscope operated at 200 kV.

III. Results

A. Cu_2O Microcrystals

Fig. 2 presented the SEM images, their corresponding TEM images of the Cu_2O nanocrystals synthesized in the media of PONPE-5 and SDS, respectively. It was shown that with the PONPE-5 mediated, the hollow sphere of copper (I) oxide were found. While the synthesis with SDS supporter, the nanocubes with truncated edges and corners were obtained.

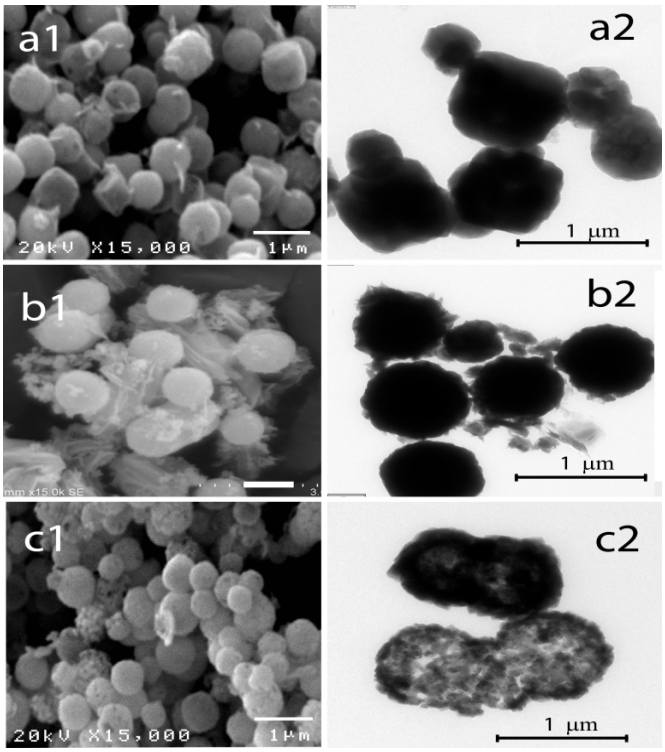

Fig. 2 SEM (1) and TEM (2) images of the Cu_2O particles (a) Synthesized with SDS at pH 7; (b) Synthesized without surfactant at pH 7 (c) Synthesized with PONPE-5 at pH 7

B. Reaction Rate Experimental

Crystal violet, $C_{25}H_{30}ClN_3$, was used as purchased from Sigma Aldrich. Sodium hydroxide (98.2%) was acquired from Mallinckrodt. 9.2 mg L-1 (2.25×10^{-5} M) of CV solution was prepared in distilled water in order to study its discoloration by NaOH. The concentration of crystal violet in the reaction mixture was selected from the absorbance of the CV at 590 nm followed Beer's law. The concentration of NaOH in the reactional mixture (0.02 M) was selected in such a way the rate of the reaction was not very slow. The study of the discoloration of CV by NaOH was carried on a double beam spectrophotometer (Varian 100).

The order with respect to CV was carried out in the presence of a large excess of NaOH. The reaction mixture was prepared as follows: 0.018 g Cu_2O micro-particles were dispersed into 20 mL of crystal violet solution 2.25×10^{-5} M. The suspension was magnetically stirred for 15 minutes to ensure adsorption equilibrium of the dye on the surface of Cu_2O crystal. Blank sample was the colorless solution prepared prior to the sample with the same procedure of the sample. Quickly after the addition of 0.5 mL of 1M NaOH, the absorbance of the solution was recorded at 590 nm every 30 second until completely discoloration of the mixtures.

Particles were identified by X-ray diffraction and the diffraction patterns were shown in Fig. 3.

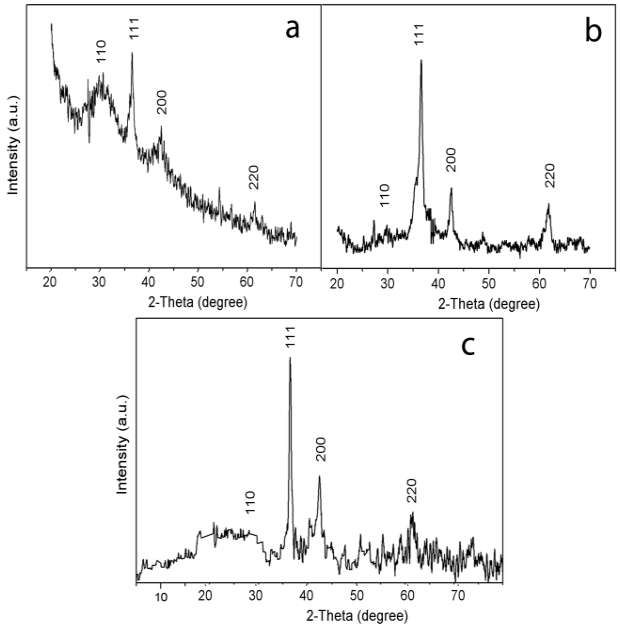

Fig. 3 Diffraction pattern of the Cu_2O particles (a) Cube Cu_2O particles (b) Sphere Cu_2O particles (c) Hollow sphere Cu_2O particles

Fig. 3 exhibited the XRD patterns of the three different morphologies of Cu_2O nanocrystals. The diffraction patterns showed clearly a coincident of major peaks fitted with the JCPDS-ICDD pattern of Cu_2O and matched with the Cu_2O produced by other methods [5], [7], [9]. As expected, nanocubes showed an exceptionally strong (200) reflection peak and a weak (111) reflection peak [10]. The intensity of the (111) peak increased progressively as nanocrystals with more {111} surfaces were formed. The (111) peak then dominates for hollow sphere [10]. Then, it was evident that the systematic morphological of the Cu_2O nanocrystals were achieved from without surfactant and with two different surfactant medias. The sizes of those particles fall mostly in

the range of 400-900 nm, so they were micrometer-sized particles.

The different morphology of Cu_2O nanocrystals was then subjected to monitor the dependence of Cu_2O shape on catalytic activity and the results were described below.

C. Kinetic Study Results

The reaction rate was based on the decolorization rate of crystal violet in the vicinity of NaOH. The concentration of CV and NaOH were fixed for all observations. Amount of catalyst was controlled by weight as mention above in the experimental section. The absorbance of the mixtures with respect to the concentration of CV versus reaction times would suggest the rate of reaction.

It should be noted that the different of reaction rate between with and without catalyst could be observed even by naked eye. To compare the reaction rate for the reaction with a variety shape of catalysts, the plots of the extent of degradation of CV versus time for all observation must be drawn and analyzed.

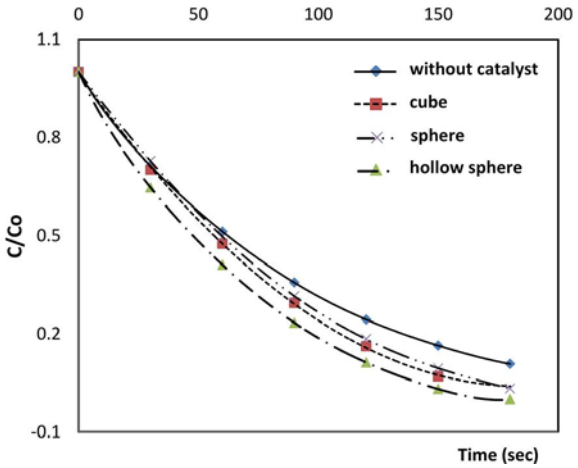

Fig. 4 A plot of the extent of degradation of CV vs. time for showing the activity with and without Cu_2O nanostructures

Fig. 4 showed clearly that the degradation of CV under catalyst process of Cu_2O was faster than that of without catalyst. The higher extent of degradation of CV by Cu_2O was attributed to the decreasing of activation energy via heterogeneous catalytic process. The comparison of catalytic reactions with different shapes of Cu_2O, cube, sphere, and hollow sphere, showed such small differ in decreasing rate. As seen from Fig. 4, the rate of reaction using Cu_2O of cube and round shape performed the coincidence of activity. It suggested of less effect of facet {111} surfaces concerned in the catalytic reaction of CV. With Cu_2O hollow sphere, the reaction showed higher decreasing rate which could be attributed to the effect of the higher surface area of the hollow structured. Upon these elementary results, it could make a conclusion that shape of Cu_2O paid no effect to the rate of reaction between CV and NaOH. The results could be completed after the determination of Cu_2O surface area.

It should be mentioned here that the photocatalytic reaction of methylene blue with Cu_2O studied by many research works [10], [16], [17] showed such a big role of the facet of {111} to elevate the rate of reaction. The contrary result was revealed that photoreaction required the reflection of light depending on the declination of molecular surface plane of catalyst whilst the simple chemical reaction requires the optimization of catalyst surface area.

The logarithm plots of CV concentration in Fig. 5 clearly showed the pseudo first order reaction of CV and NaOH when the reaction underwent without catalyst. Deviation from straight line was found in the reaction underwent with catalyst. It was attributed to the measurement of absorption in the vicinity of nanoparticle catalysts which probably made some interferences of absorption.

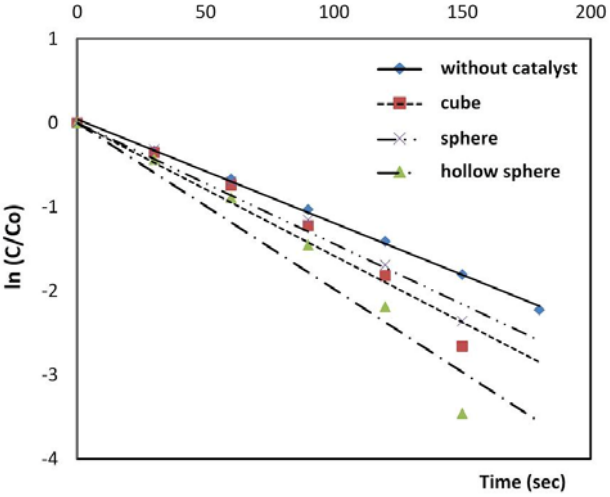

Fig. 5 A plot of ln(C/Co) versus time

Here in Fig. 5, as expected, hollow sphere of copper oxide must serve as the efficient catalyst with respect to its higher surface area rather than its morphology. This confirmed that the reaction rate does not depend on shape of copper oxide and should favor on the total surface area of the catalyst as mentioned elsewhere [18].

A point of view was purposed here that the discoloration rate between CV and NaOH is a fast reaction with completely depends on the concentration of reactants. The presence of catalyst could not show the significant responses on the fast reaction. Therefore, the possibility to study the effect of different shapes of copper oxide must be confirmed with some other suitable reactions which deserve some further studies.

IV. Conclusion

The preparation of Cu_2O nanostructures with the shape of cubic and hollow sphere structures was successful in the presence of SDS and PONPE-5, respectively. Sphere shape was obtained in the absence of any surfactant. Those crystals were micrometer-sized. The crystals were characterized by SEM, TEM, and XRD techniques. For reaction rate study, crystals of Cu_2O with different shapes exhibited good catalytic activity toward the degradation of crystal violet but could not

observed role of shapes on rate of reaction. Focus on the use of Cu_2O nanoparticle, it was expected to have more insight into the catalytic properties of Cu_2O which can be provided by using these crystals with well-defined structures.

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